**Hydrothermal CO2 Reduction and Biomass Valorization in One-Pot Reaction.**

María Andérez-Fernández,1\*Gareth Davies,2 Justin Driver,2 Cynthia Kartey,2 Eduardo Pérez,1 Ángel Martín,1 James McGregor,2 M. Dolores Bermejo,1

*1BioEcoUva. Research Institute on Bioeconomy. High Pressure Process Group. Department of Chemical Engineering and Environmental technology. Universidad de Valladolid, Valladolid, 47011, Spain, Spain*

*2Department of Chemical Engineering, University of Sheffield, Sheffield, S1 3JD, United Kingdom*

*\*Corresponding author: mariaanderezfernandez@gmail.com*

**Highlights**

* It is the first time that NaHCO3 hydrothermal reduction is performed using non-edible biomass.
* A higher extent of liquefaction of biomass was achieved by adding NaHCO3.
* Biomass with high-content in holocelluloses (sugar bagasse) achieved higher yields.

**1. Introduction**

Production of fuels and chemicals from renewable sources is extensively investigated due to the low level of fossil fuels reserves and their impact on environment. Among the different technologies hydrothermal valorization of lignocellulosic biomass has been intensely investigated. High temperature water (HTW) exhibits outstanding properties c, playing different roles in the reaction, such as reactant, solvent and catalyst.

Increasing carbon dioxide (CO2) levels are having harmful consequences for the environment. Different processes have been envisioned as effective methods for CO2 conversion into useful chemicals and fuels, being hydrothermal processing one of the most innovative. CO2 hydrothermal reduction has already been studied using metals and organic model compounds1,2. Combining both processes of hydrothermal biomass valorization and hydrothermal CO2 reduction to produce useful chemicals would lead to an optimized and greener process.

In this research, CO2 conversion to formic acid in hydrothermal media was carried out using non-edible lignocellulosic biomass (pine needles and sugarcane bagasse), demonstrating the possibility for the first time the use biomass residues as a reductant for CO2 reduction in a one-pot reaction.

**2. Methods**

Reactions were performed in a 100 mL batch reactor with a magnetically driven impeller. Biomass (pine needles, PN, or sugarcane bagasse, SB) were presoaked overnight in 25mL of distilled water, and placed afterwards in the reactor, adding extra 25 mL of water and sodium bicarbonate (NaHCO3)as a CO2 source. After sealing and purging the reactor, the reactor was placed in a heating jacket, previously preheated, and setting this point as t=0’. After the desired reaction time, the reactor was cooled and liquid and solid samples were collected. Liquid samples were analyzed using HPLC and TOC techniques, while solid samples were analyzed through FTIR and SEM.

**3. Results and discussion**

To study whether biomass residues can convert NaHCO3 into formic acid in one-pot reaction, both PN and SB were treated with and without NaHCO3 for 30 min at 250ºC (0.50M NaHCO3 and 1.0g of biomass). Results showed that not only a higher production of formic acid when NaHCO3 was added in both cases, but also to a higher content of dissolved organic carbon in liquid samples, achieving a higher extent of biomass liquefaction. Comparing both biomass types, SB achieved a better yield to formic acid (referenced to the initial amount of biomass) than PN. This may be caused by a higher amount of holocelluloses (sugar-based biopolymers) in SB than in PN.



**Figure 1.** Influence of the amount of initial SB at 250ºC for 30 min.

Thus, selecting SB as reductant, different reaction parameters were optimized, such as initial amount of biomass (0.10g, 0.25g, 0.50g and 1.00 g, results shown in Figure 1), temperature (225ºC, 250ºC and 275ºC) and time (15 min, 30 min, 60 min, 90 min and 180 min). The best yield to formic acid was achieved using 0.25 g of SB in a 50 mL solution of 0.50M NaHCO3 at 250ºC for 180 min (0.10g of formic acid per gram of initial sugar bagasse). Among the different by-products resulting from the biomass liquefaction and hydrolysis, acetic acid, lactic acid, glycolaldehyde and glyceraldehyde were detected in the highest concentrations.

**4. Conclusions**

For the first time, the possibility of converting NaHCO3 as CO2 in hydrothermal media was accomplished using biomass residues. Despite future work should study in the mechanism of the reaction and the implementation of the processes in a continuous pilot plant, this work is a promising starting point for a novel method of CO2 and biomass valorization.

**Acknowledgments**

This project has been funded by Junta de Castilla y León through project VA248P18. MAF acknowledges Junta de Castilla y Leon for predoctoral position (Orden EDU/520/2017). MDB thanks MINECO for Ramon y Cajal position.

**References**

1. Z. Shen, Y. Zhang, F. Jin, Green Chem. 13 (2011) 820-823
2. M. Andérez-Fernández, E. Pérez, A. Martín, M.D. Bermejo, J. Supercrit. Fluids 133 (2018) 658-664